

Enhanced dispersion of MWCNTs and synergistic properties in multiphase epoxy nanocomposites by incorporation of inorganic nanoparticles

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Abstract. In the present work we report that the addition of inorganic nanoparticles to MWCNT epoxy composites leads to the formation of a hybrid structures which cause different states of dispersion for the multiphase nanocomposites containing either MWCNTs and titania or MWCNTs and silica. The microstructure is characterised by titania nanoparticles attached to the surface of MWCNTs leading to an enhanced dispersion of MWCNTs. The hydrophilic surface of fumed silica nanoparticles causes the formation of independent networks of silica and MWCNTs. Therefore, the change of the state of dispersion is less pronounced compared to the MWCNT/titania structures.

Changes in the state of dispersion lead to a decrease in electrical conductivity for the MWCNT/titania systems. Conversely, an almost independent behaviour was found for the MWCNT/silica nanocomposites due to their interpenetrating networks. Besides the altered state of dispersion, the hybrid structure leads synergistic effects in terms of the glass transition of the nanocomposites. Although a decrease of the glass transition temperature (T_g) is observed for the nanocomposites containing only one kind of filler, the combination of nanoparticles can reduce the decrease of T_g .

Introduction

The potential to significantly modify the properties of polymers depends strongly on the physical nature of each type of nanoparticle. Inorganic particles such as fumed silica or titania mostly affect the mechanical and functional properties of polymers [1-4]. Among all types of nanoparticles carbon nanotubes gained high interest in the last decade due to their unique combination of good mechanical and electrical properties [5]. Depending on the processing route and type of carbon nanotubes, percolation thresholds could be found below 0.1 wt.-% in epoxy matrix systems [6-8]. The control of carbon nanotube dispersion and its improvement still remains a great challenge due to their very high specific surface area (up to 1300 m²/g).

In this work, a new approach was conducted for an altered state of carbon nanotube dispersion by the addition of a second type of nanoparticle, which constitute a third phase. One major advantage of such multiphase systems is the enhanced dispersion combined with improved physical properties due to synergistic effects [9].

Experimental

The used polymer matrix consists of an epoxy resin (LY 556 by Huntsman[®]), cured with an anhydride hardener and accelerator. The used nanoparticles are multi-wall carbon nanotubes (MWCNTs), fumed silica and titania. The MWCNTs exhibit an outer diameter of 15 nm with length up to 10 μm, supplied by Arkema[®]. AEROSIL[®] 380 is a hydrophilic fumed silica,

constituted by primary particles with an average diameter of 7 nm, supplied by Degussa-Evonik. The titania nanoparticles (Hombitec[®] RM110) consists of primary particles with an average diameter of 10 nm supplied by Sachtleben[®]. Binary (one type of particle) and ternary nanocomposites (two types of particles) were produced with a three-roll-mill as mentioned elsewhere [4,6]. Only combinations of MWCNTs with titania or silica were produced. For the binary systems the volume content of the fillers was varied from 0.01, 0.1 to 0.3, respectively. For the multiphase systems the volume content was kept constant for one type of filler and varied for the other one as mentioned before, e.g. 0.01 vol.-% MWCNT plus 0.01 vol.-% titania. Additionally, binary systems with 0.6 vol.-% filler content were produced as references. Table 1 shows the produces sample matrix.

Table 1. Overview of the produced nanocomposites.

vol.-%		Titania or silica				
		0	0.01	0.1	0.3	0.6
MWCNT	0	x	x	x	x	x
	0.01	x	x	x	x	
	0.1	x	x	x	x	
	0.3	x	x	x	x	
	0.6	x				

After curing (4 hours at 80°C and 8 hours at 140°C), samples were prepared for impedance spectroscopy. The electrical conductivity values used for comparison were taken at 1 kHz. Thermal analysis was performed with a Seiko[®] SCC 5200 differential scanning calorimeter (DSC). After curing process in the DSC chamber, the glass transition temperature (T_g) was determined in a second heating scan at a rate of 10°C/min. The light micrographs were taken in transmission mode at a magnification of 50 with a standard Leitz[®] light microscope. Transmission electron micrographs were taken using a Philips EM 400 at 120 kV.

Results and Discussion

Nanocomposites morphology

Figure 1 shows the multiphase structures of the produced nanocomposites. For the MWCNT/titania systems primary particles of titania cover the surfaces of nanotubes (see figure 1.b). Agglomerates of titania surround agglomerates of MWCNTs (see figure 1.a). It has to be mentioned that only fully separated agglomerates can be interpenetrated by titania nanoparticles. Some agglomerates which derive from the previous CVD-production process are condensed and physically entangled (see figure 1.b). They can neither be separated by the high shear mixing process nor by the incorporation of titania. Therefore, titania can act only as a dispersing agent to free movable MWCNTs. Nevertheless, the strong affinity of titania to aromatic rings (graphite-like structure) can cause the hybrid structure [10]. Another important effect of such interactions between MWCNTs and titania is related to the zeta-potential of the titania nanoparticles. In organic solvents as epoxy MWCNTs are reported to have a positive surface charge while titania tend to possess a negative surface charge in the presence of carboxylic acids such as the anhydride hardener [11,12].

Unlike titania, the hydrophilic nature of silica leads to a simultaneous formation of co-existing silica and MWCNT networks in the ternary nanocomposite (see figure 1.c). It is known that the mismatch in surface characteristics leads to the formation of silica and carbon domains in polymers [13]. Thus, the hybrid structure differs significantly compared to those of MWCNT/titania systems. The specific interparticle interactions of titania or silica to MWCNTs also lead to changes in the spatial distribution of the MWCNT agglomerates which can be found in the presented poster.

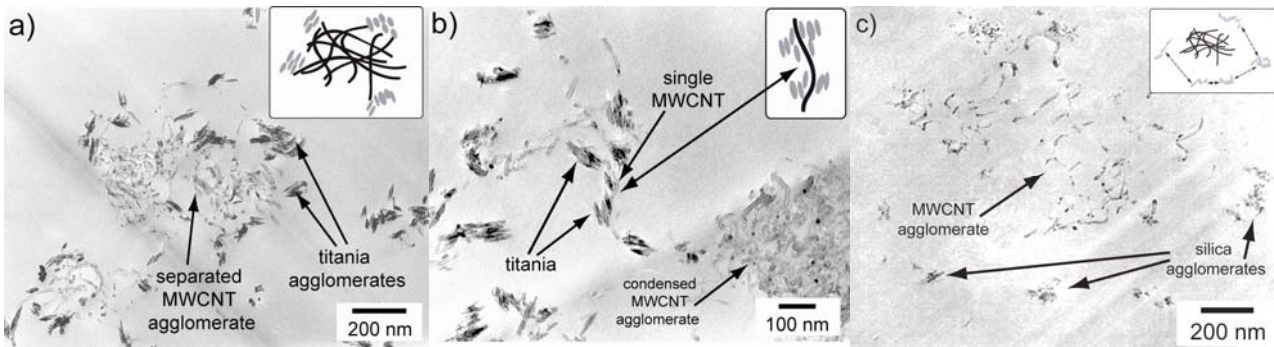


Figure 1. TEM micrographs of a), b) MWCNT/titania and c) MWCNT/silica [14]

Electrical conductivity

The electrical conductivity results are presented in figure 2. Carbon nanotubes exhibit an electrical percolation behaviour which is characterised by an abrupt increase in electrical conductivity by orders of magnitude since a network of carbon nanotubes is built up [7]. The formation of such a network is strongly dependent on the type of filler, functionalisation, dispersion process and curing conditions. Therefore, the presence of inorganic particles may lead to changes in the electrical conductivity.

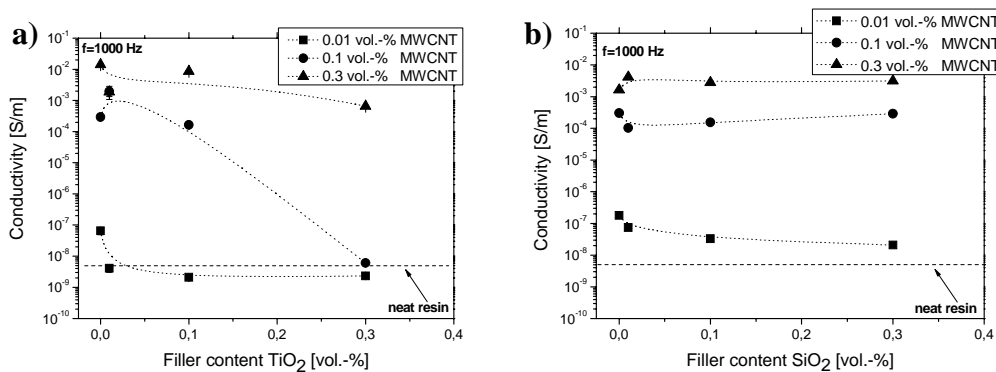


Figure 2. Electrical conductivity as a function of filler content of non-conductive particles, a) MWCNT/titania, b) MWCNT/silica [14]

Titania decreases the electrical conductivity because of an improved state of dispersion of MWCNTs. For the ternary nanocomposites containing 0.01 vol.-% MWCNT the electrical conductivity values level off as the titania load is increased. A similar trend was observed for the ternary nanocomposites containing 0.1 vol.-% MWCNT. If the amount of titania (0.3 vol.-%) exceeds the amount of carbon nanotubes (0.1 vol.-%) a decrease of several orders of magnitude was observed.

Conversely, an almost titania-independent conductivity was found for the ternary systems with 0.3 vol.-% MWCNT. Here, the addition of titania only leads to a maximum decrease to 10⁻³ S/m. In principle, systems containing higher amounts of carbon nanotubes do not react as sensitive to the addition of titania as the low filled systems.

Silica exhibit a different influence on the state of dispersion compared to titania as mentioned previously. The addition of silica does not lead to a significant change in electrical conductivity. For the low filled systems with 0.01 vol.-% MWCNT the conductivity does decrease with increasing silica content, but not as pronounced compared to the MWCNT/titania composites. For higher filled MWCNT systems the addition of silica even leads to slight increases in electrical conductivity.

The differences in the development of electrical conductivities of the MWCNT/titania and MWCNT/silica systems can be explained in terms of different hybrid microstructures. Titania is mostly situated at the vicinity of MWCNTs or MWCNT agglomerates. Thus, the statistical amount of network contacts is reduced. Additionally, the tunnelling distance between two MWCNTs increases or even lead to a total disruption of electrical contact. The tunnelling turns out to be the driving mechanism for the development of electrical conductivity in filled polymers. Unlike titania, silica builds up an independent network which leads to formations of MWCNT and silica domains. Here, the effective volume content of MWCNT is increased due to the occupied volume of silica without changing the MWCNT network [15].

Synergistic effects regarding glass transition temperature

Figure 3 shows the glass transitions temperatures of the produced nanocomposites. The addition of MWCNTs subsequently decreases the T_g up to 10 °C compared to the neat resin (see figure 3.a). A similar behaviour is found for the binary systems with titania or silica. In case of titania the addition of 0.6 vol.-% leads to a decrease of 16 °C. The behaviour of the ternary systems differs significantly from the binary systems and is strongly depended on the filler concentrations of each type of particle. Thus, a quite inconsistently behaviour is found. Nevertheless, in case of the ternary systems with 0.3 vol.-% MWCNT the negative influence of titania is almost counteracted by the MWCNTs (figure 3.a right columns), since a decrease in T_g with increasing titania content cannot be observed. Additionally, in ternary MWCNT/titania systems increasing filler content of MWCNTs leads to increases in T_g contrary to the binary MWCNT systems.

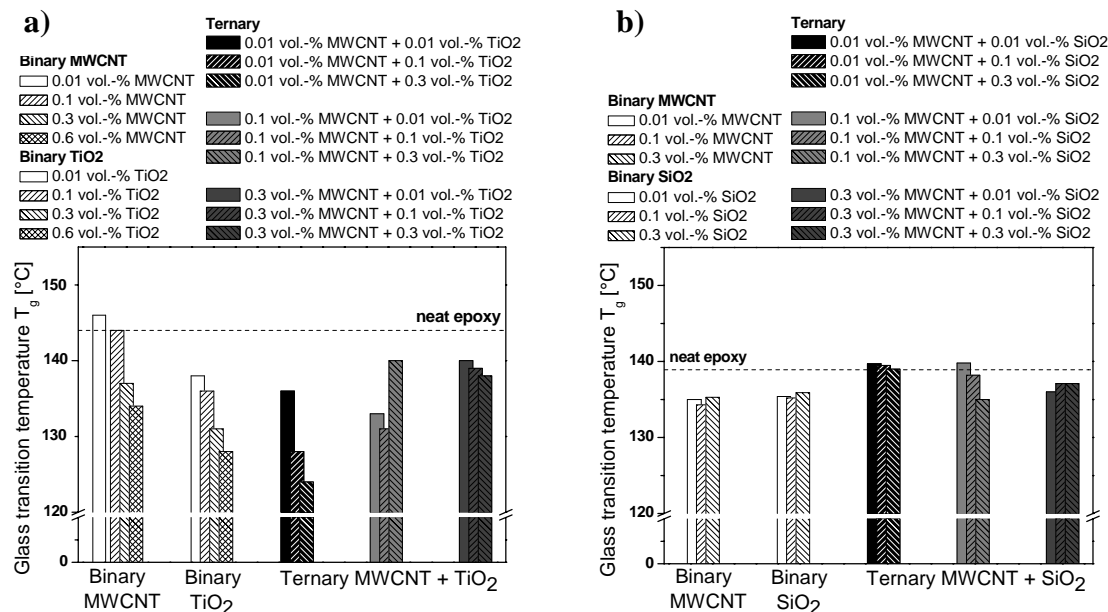


Figure 3. T_g of the multiphase nanocomposites, a) MWCNT/titania, b) MWCNT/silica [14]

For the MWCNT/silica systems the behaviour is less pronounced compared to the MWCNT/titania systems. Here, the ternary nanocomposites exhibit higher or even constant T_g . Almost no change of T_g was found for increasing filler contents of both silica or MWCNTs. Changes in T_g in nanocomposites are mainly attributed to the formation of an influenced matrix region in the vicinity of the nanoparticles, often reported as interphase [16]. The size and properties of the interphase are strongly depended on the matrix polymer, the interface chemistry of matrix and particles, and the state of dispersion by means of the effective interfacial area between particles and matrix.

Besides changes in the state of dispersion, we believe that possible interactions between particles and hardener/resin cause changes in the stoichiometry of resin and hardener in the interphase region, and thus a decrease in T_g is observed. Aromatic rings of the epoxy can interact strongly with the graphitic layers of MWCNTs, leading to a selective adsorption of the resin since the anhydride hardener does not contain any benzene-like structure [17,18]. Titania might de-activate the anhydride giving rise to materials having a lower cross-linking density [19]. Silica itself does not exhibit strong chemical interactions with the anhydride but can interact either with the resin or with the hardener via hydrogen bonding. Thus, the decrease in T_g is lower, giving rise to lower synergistic effects in ternary systems compared to the MWCNT/titania systems.

Summary

Ternary epoxy nanocomposites based on MWCNTs and titania or silica are successfully produced leading to the formation of multiphase structures. Due to intrinsic chemical interactions between the MWCNTs and the titania nanoparticles a hybrid structure is formed without any additional functionalisation of the nanoparticles leading to an improved state of dispersion for low filled MWCNT nanocomposites. Due to the formation of a silica network in the MWCNT/silica ternary systems the hybrid structure is characterised by the formation of domains of each type of nanoparticles leading to an almost constant state of dispersion of MWCNTs. Changes in dispersion state were monitored by impedance spectroscopy. In case of MWCNT/titania increasing titania contents decrease conductivity. In case of MWCNT/silica increasing silica contents lead to constant or even slightly increased electrical conductivities. Chemical interactions between particles as well changes in the state of dispersion lead to synergistic effects in interphase formation characterised by a suppression of the decrease of the glass transition temperature in the ternary nanocomposites.

References

- [1] B. Wetzel, P. Rosso, F. Hauptert, K. Friedrich: *Eng. Fract. Mech.* 37 (2006) p. 2375.
- [2] B.B. Johnsen, A.J. Kinloch, R.D. Mohammed et al.: *Polymer* 48 (2007) p. 530.
- [3] V.M.F. Evora, A. Shukla: *Mat. Sci. Eng. A* 361 (2003) p. 358
- [4] M.H.G. Wichmann, M. Cascione, B. Fiedler et al.: *Compos. Interfaces* 13 (2006) p. 699
- [5] M. Moniruzzaman, K.I. Winey: *Macromolecules* 39 (2006) p. 5194
- [6] F.H. Gojny, M.H.G. Wichmann, B. Fiedler et al.: *Polymer* 47 (2006) p. 2036
- [7] J.K.W. Sandler, J.E. Kirk, I.A. Kinloch et al.: *Polymer* 44 (2003) p. 5893
- [8] M.B. Bryning, M.F. Islam, J.M. Kikkawa, A.G. Yodh: *Adv. Mater.* 17 (2005) p. 1186
- [9] L. Liu, J.C. Grunlan: *Adv. Funct. Mater.* 17 (2007) p. 2343
- [10] Y. Yang, P. Wang: *Polymer* 47 (2006) p. 2683
- [11] P. Bing, H. Yi, C. Li-Yuan et al.: *J. Cent. South. Univ. Technol.* 14 (2007) p. 490
- [12] H.-F. Wei, G.-H. Hsiue, C.-Y. Liu : *Comp. Sci. Technol.* 67 (2007) p. 1018
- [13] M.-J. Wang: *Rubber Chem. Technol.* 71 (1997) p. 520
- [14] J. Sumfleth, L.A.S.A. Prado, M. Sriyai, K. Schulte : *Polymer*, submitted.
- [15] W. Zhang, R.S. Blackburn, A.A. Dehghani-Sani: *Scr. Mat.* 56 (2007) p. 581
- [16] L. Schadler, L.C. Brinson, W. Sawyer: *JOM* 59 (2007) p. 53
- [17] K.E. Wise, C. Park, E.J. Siochi, J.S. Harrison: *Chem. Phys. Lett.* 391 (2004) p. 207
- [18] A. Star, T.-R. Han, J.-C.P. Gabriel, K. Bradley, G. Grüner: *Nanoletters* 3 (2003) p. 1421
- [19] U. Diebold: *Surf. Sci. Rep.* 48 (2003) p.53